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(54) Synthetic polymeric adsorbents and ion exchange resins, their production and processes using them.

(57) Synthetic polymeric adsorbents are produced from lightly crosslinked macroreticular aromatic copolymer beads by post crosslinking the copolymer beads while in a swollen state, the crosslinks resulting from the post-crosslinking comprising the residue of external crosslinker selected from polyfunctional alkylating agent, polyfunctional acylating agent and sulfur halide. A Friedel-Crafts catalyst may be used for the post-crosslinking. The adsorbents may be functionalized to produce ion exchange resins. The adsorbents are generally useful in processes for removing components from fluids by adsorption, particularly in adsorbing organic components from liquid or gas streams. The ion exchange resins are useful not only in ion exchange processes in general but may also be useful as catalysts.

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SYNTHETIC POLYMERIC ADSORBENTS  
AND ION EXCHANGE RESINS, THEIR PRODUCTION  
AND PROCESSES USING THEM

5 This invention is concerned with synthetic polymeric  
adsorbents and ion exchange resins, methods of preparing  
them and catalysis, adsorption and ion exchange processes  
using them, for example water-treatment processes,  
processes for the recovery of organic materials from  
gaseous and other streams and pharmaceutical purification  
10 processes.

Adsorbents are usually solids which exhibit  
selectivity at their surface for substances in a fluid  
mixture, thereby providing a means of separating such  
substances from the mixture. The high surface area  
15 characteristic of adsorbents (usually well above  $5\text{m}^2/\text{g}$   
of solid) normally results from a fine state of subdivision  
(non-porous adsorbents) or from pores in the adsorbent  
particles (porous adsorbents). Carbon black and  $\text{TiO}_2$  and  
 $\text{ZnO}$  pigments are examples of non-porous adsorbents.  
20 Granular carbon, silica gel, bone char, certain soils and  
asbestos are examples of well-known porous adsorbents  
obtained from naturally occurring materials. For  
separation or purification of complex substances (such  
as pharmaceuticals) synthetic polymeric adsorbents have  
25 been developed, some of which serve also as ion exchange  
materials or as intermediates for the manufacture of ion  
exchange materials. However, ion exchange is an  
adsorption as well as an adsorption phenomenon, so that  
although all ion exchange materials are adsorbents, the  
30 converse is not necessarily true.

Synthetic adsorbents are usually porous polymeric  
solids, polystyrene and styrene-divinylbenzene copolymers  
being representative. Although it is possible to  
prepare fine particle size synthetic polymers directly  
35 or by grinding larger particle size polymers to a fine  
particle size to obtain high surface area, fine particle  
size adsorbents cannot be used in cyclic processes,  
particularly processes involving adsorbent beds in columns,

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since the fine particles pack too tightly and impede fluid flow. Adsorbents of moderately large particle size, about 0.02 mm. to 2 mm. diameter or greater, are therefore required. Polymeric beads, obtained by known suspension polymerization techniques, have a convenient particle size for use in columnar operations. Nevertheless, although the polymeric adsorbents can be made hydrophobic and the bead form enhances the usefulness of the polymeric adsorbents, their adsorbent properties have been somewhat unattractive in comparison with the carbonaceous adsorbents obtained from the pyrolysis of organic materials. However, the latter tend to suffer from high moisture pick up in humid atmospheres, from poor reproducibility during manufacture, and from such fine pores and rigid structure as to make them vulnerable to cracking, splitting and decr ipitation under high osmotic pressures such as are often encountered in cyclic operations.

The preferred resins of this invention have a good balance of the desirable properties of these prior art resins and avoid their most serious deficiencies. In this regard, even though certain of the adsorbents of this invention may lack the extremely high surface areas of the known polymeric adsorbents or activated carbon adsorbents, they may still equal their performance, especially in adsorption capacity for organic liquids at high concentration.

The adsorbents of the invention are polymeric materials in macroreticular bead form which, when functionalised, form ion exchange resins of the invention. The beads are produced by swelling lightly crosslinked macroreticular aromatic polymer beads in an inert organic solvent, and then post-crosslinking the polymer by contacting the swollen beads with one or more of the following crosslinkers: polyfunctional alkylating or acylating agents and sulfur halides. A Friedel-Crafts type acid catalyst is used for the post-crosslinking. Typically, the adsorbents have surface areas in the range of about 100-1400 m<sup>2</sup>/g and porosities of at least

0.2 m<sup>3</sup>/m<sup>3</sup>, more usually 0.3 - 0.6.

The adsorbents are called "macronets" because the crosslinks are stable and have a long and rigid structure. Such structure results from post-crosslinking swollen  
5 lightly crosslinked polymer substrates, the swollen state causing displacement of the polymer chains to significant distances from each other. The use of macroreticular polymer substrates as the beads for swelling and cross-  
10 linking in the invention greatly enhances the porosity and adsorbent properties of the products. The term "macronet" has previously been used to describe the ion exchange functionalized polystyrene and styrene-divinylbenzene copolymer macromolecules obtained by crosslinking linear  
15 polystyrene in solution or styrene polymers in the swollen state by reaction with an alkylating agent under Friedel-Crafts conditions, as described in U.S. Patent 3,729,457 and in related articles in The Journal of Polymer Science, Symposium No.47, pages 95 - 101 and 189 - 195 (1974).  
20 Similar ion exchange resin products are disclosed in British Patent 1,095,746 wherein polystyrene or a styrene derivative in a swollen pearl form undergoes crosslinking by acylation under Friedel-Crafts conditions. In these prior art reactions, a macronet product is obtainable but, the use of the macroreticular polymer bead form is not  
25 contemplated. The use of this macroreticular form in this invention gives products of better performance and enhanced economy.

The term "macroreticular" (as opposed to "microreticular") is well known in the art and depicts porous  
30 adsorbents in which the pores are larger than atomic distances and are not part of the polymer structure per se. Rather, the pores are microscopic channels and in most cases they result from the formation of the polymer beads in a suspension polymerization in the presence of a phase  
35 extender which acts as a solvent for the monomer mixture is chemically inert under the polymerization conditions and exerts so little solvating action on the product polymer that phase separation of the product polymer takes place.

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This results in "squeezing out" of the organic precipitant (phase extender) from the copolymer mass. As a consequence, the pore structure is not dependent upon ambient conditions and therefore is retained despite contact with various concentrations of electrolyte, solvent and exchangeable ions. In "microreticular" (gel-type) adsorbents the "pores" are not true pores being extremely small, usually below  $30 \times 10^{-10} \text{m}$  in diameter, and will disappear from the polymer structure when the polymer is dried. Because the pores of macroreticular resins are relatively large and are not greatly influenced by changes in ambient conditions, the macroreticular polymers are able to withstand large osmotic pressure variations commonly encountered in cyclic processes. Moreover, their moderately large particle size makes them especially useful in operations utilizing columns particularly in their ion exchange form, where the molecular weight of an ionic species to be exchanged is so high as to exclude use of gel-type ion exchange resins. Macroreticular polymers for ion exchange resin use are described in the technical literature, as in U.S. Patents 3,037,052, 3,637,535 and 3,843,566.

The lightly crosslinked macroreticular aromatic copolymer beads used in forming the macronet adsorbents and ion exchange resins of the invention are a well known class of materials as exemplified in the U.S. patents just listed and in other patents and publications, and many are commercially available. Accordingly, only a brief description of these materials is necessary.

In summary, the macroreticular substrate polymers are lightly crosslinked copolymers usually of (1) polyunsaturated monomer, containing a plurality of non-conjugated  $\text{CH}_2 = \text{C} <$  groups, which acts as a crosslinking agent, and (2) monoethylenically unsaturated monomer. At least one of the polyunsaturated and monoethylenically unsaturated monomers is usually aromatic, and preferably both are aromatic, provided that a major proportion of the copolymer (at least 50% by weight) comprises aromatic units. For

light crosslinking, sufficient of the polyunsaturated monomer will be used to give dimensional stability to the copolymer bead so that it will swell rather than dissolve in the subsequent swelling step. Suitable amounts of such crosslinking monomers are from 0.25 to 20% by weight of the monomer mixture, preferably closer to the lower end of this range, for example 0.5 to 8% and more usually 1 - 4%. The preferred polyunsaturated monomers include divinylbenzene and trivinylbenzene and the preferred monoethylenically unsaturated monomers include styrene, the o, m, and p-methyl styrenes, the o, m, and p-ethyl styrenes, ethylvinylbenzene, vinylnaphthalene and vinyltoluene. While hydrocarbon monomers are preferred, the monomers may also include hetrocyclic compounds such as divinylpyridine. Among the suitable aliphatic polyunsaturated monomers may be mentioned diacrylates and dimethacrylates, such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, neopentyl glycol dimethacrylate, divinylketone, divinyl sulfide, allyl acrylate, diallyl maleate and diallyl fumarate. Suitable monoethylenically unsaturated aliphatic monomers include esters of acrylic acid, such as methyl, ethyl and propyl acrylate, and the corresponding esters of methacrylic acid, wherein the ester group contains 1 - 10 carbon atoms. The preferred macronet adsorbents of the invention are based on macroreticular copolymers of styrene and divinylbenzene (about 99 - 80 wt. % styrene, balance divinylbenzene) and copolymers of styrene (about 40 - 60 wt %), vinylbenzyl chloride (about 40 - 60 wt %) and divinylbenzene (about 1 - 20 wt %). The foregoing ranges are on the basis of 100% active monomers. When commercial grades of divinylbenzene are used, about 20 - 50% of the divinylbenzene is ethylvinylbenzene and it is conventional to include the ethylvinylbenzene with the styrene or other monovinyl monomer when specifying the proportion of styrene or other monovinyl monomer. The polymers may contain minor amounts of other monomers, such as about 1-4% by weight of acrylonitrile.

As mentioned above the macroreticular polymers are most usually prepared under suspension polymerization conditions utilising a free radical catalyst and a liquid precipitant (phase extender) which acts as a solvent for the monomer mixture and which is present in such amount as to exert such small solvating action on the product crosslinked copolymer that phase separation of the product copolymer takes place as evidenced by the fact that the product copolymer is no more than semi-transparent and is preferably opaque when associated with a fluid having a different refractive index. The precipitant is chemically inert under the polymerization conditions and its selection will be determined by the character of the monomers in the monomer mixture. When employing the preferred aromatic hydrocarbon monomers of the invention, such as styrene, divinylbenzene and ethylvinylbenzene, alone or with vinylbenzyl chloride, the precipitant may be an alkanol containing 4 - 10 carbon atoms, such as methylisobutylcarbinol, or it may be a saturated aliphatic hydrocarbon containing at least 7 carbon atoms, such as heptane, isooctane and cyclohexane.

When suspension polymerization is the polymerization method used, the precipitant must be either immiscible or only partially miscible with the suspending medium.

Other monomer compositions from which the macroreticular copolymers may be formed are described in U.S. Patent 3,991,017 and in U.S. Patents 3,275,548 and 3,357,158 and British Patents 932,125 and 932,126.

After formation of the macroreticular polymer the polymer is swollen in an inert organic solvent. Optionally the swelling and polymerization process may be carried out simultaneously if the precipitant is a swelling solvent. A variety of solvents and solvent mixtures may be used as swelling solvent, including chlorinated hydrocarbons such as chlorobenzene, ethylene dichloride, perchloroethylene, propylene dichloride, and dichlorobenzene; aliphatic hydrocarbons, such as hexane, isooctane and petroleum ether; nitro paraffins such as ni-

propane; nitro aromatics such as nitro benzene; and miscellaneous solvents such as carbon disulfide. Ethylene dichloride is the preferred solvent.

5 While the copolymer is in the swollen state and is in the swelling solvent, the crosslinking is carried out, conveniently by adding Friedel-Crafts catalyst and crosslinking agent and heating the mixture to 40-100°C. or higher (depending on the boiling point of the solvent) for 1 to 24 hours. Other reaction temperatures and times may be used, depending upon the reactive species and catalyst in the reaction mixture. Following reaction, 10 the reaction mixture may be quenched with water or a lower alkanol such as methanol, or acetone, or by inverse aqueous quenching and the product macronet polymer beads separated 15 by thorough washing with suitable solvents and drying.

Friedel-Crafts polyfunctional alkylating agents give the best products but useful macronet adsorbents are also prepared with Friedel-Crafts polyfunctional acylating agents and with inorganic sulfur halides. The suitable polyfunctional alkylating agents include polyhalides, polyols 20 and polyolefins, such as  $\alpha$ ,  $\alpha$ -dichloro-p-xylene, polyvinyl chloride, methylene chloride, chloromethyl methyl ether, bis(chloromethyl)benzene, bis 1,4-chloromethyl biphenyl, bis(chloromethyl)thiophene, 1,4-dichlorohexane, 1,4-dichlorobutane, chloroform, carbon tetrachloride, 25 paraldehyde, alkylene glycols such as ethylene glycol, diepoxides and polybutadienes. It will be apparent that the alkylating agents may contain aromatic groups provided the atoms of the alkylating agents which bond to the macroreticular polymer are aliphatic carbon atoms. 30

The difunctional acylating agents preferably are aromatic compounds but aliphatic compounds are also useful. Generally, the acylating agents are diacid chlorides although polyesters and polyamides are also useful. In 35 the case of the aromatic diacid chlorides, the carbonyl groups must be separated by at least one carbon atom. For example, while suitable aromatic diacid chlorides include terephthaloyl chloride and isophthaloyl chloride, ortho-phthaloyl chloride would not be suitable since it tends



to form anthraquinone rings which in turn participate in redox reactions.

Other suitable acylating agents include 1,4-naphthoyl dichloride, 1,5-naphthoyl dichloride, 1,6-naphthoyl dichloride, anthracene-1,5-diacid chloride, anthracene-1,9-diacid chloride, chlorofumaric acid, dichloromaleic acid, and the dichlorides of malonic, succinic, adipic and sebacic acids. Still other acylating agents include phosgene and thiophosgene. The inorganic sulfur halide crosslinkers are liquids under the reaction conditions and include sulfur monochloride, sulfur dichloride and the corresponding bromides.

Any Friedel-Crafts type catalyst may be utilised to catalyze the reaction, such as acidic metal halides, including aluminum chloride, stannic chloride (preferred), aluminum bromide, boron fluoride, zinc chloride and ferric chloride. The swelling solvent and the solvent selected for the reaction medium, if an additional solvent is used, may be the same or different but should be solvents which will not deactivate the Friedel-Crafts catalyst. The swelling solvents set forth above have this character. From about 0.001% to about 5% by weight of catalyst based on polymeric substrate will be effective, but the optimum amount of catalyst will depend upon the reactants and conditions of the reaction.

The crosslinking agent added to the reaction mixture effects "external" (sometimes called "secondary") crosslinking, as contrasted with crosslinking which may occur internally between monomers in the polymer backbone which will crosslink in the presence of a Friedel-Crafts catalyst. One such monomer is vinylbenzyl chloride. The combination of external and internal crosslinking is also a preferred feature of the polymers in the invention, as demonstrated hereinafter.

If desired, the macronet adsorbents may be converted to ion exchange resins by known techniques. For example, the adsorbents may be converted to weak base resins by chloromethylation (if not based on vinylbenzyl chloride) and then aminolysis with dimethylamine, or to strong base

resins by chloromethylation (if required) and then amination with trialkyl amines such as trimethylamine. Likewise, certain of the adsorbents may be converted to acidic cation exchange resins by sulfonation or phosphorylation. It will be understood that the more highly crosslinked the macronets the less useful are they likely to be as intermediates for ion exchange resin formation. However, if the crosslinking agents are aromatic or otherwise provide bulky crosslinks, the macronets products may still exhibit good ion exchange capacity upon functionalization to ion exchange form, even though highly crosslinked. Accordingly, a balance is required between crosslinking density and crosslink bulk for use of the macronets in ion exchange resin formation. Functionalizing of polymeric adsorbents to form ion exchange resins is well-known and therefore requires no further elaboration. The patents listed above provide good description of ion exchange resin formation. One form each of adsorbent and ion exchange resins of the invention results when the macronet adsorbents are used as substrates in the formation of hybrid copolymers and ion exchange resins in accordance with U.S. Patent 3,991,017. Briefly, in forming hybrid copolymers and ion exchange resins, a liquid monomer mixture containing a crosslinking monomer is added to an aqueous suspension of the macronet adsorbent, which liquid monomer mixture is imbibed into the pores of the macronet adsorbent and is polymerized therein. The resulting hybrid product may then be converted to an ion exchange resin by appropriate functionalization in the conventional manner. If the macronet adsorbent and / or the imbibed monomer mixture contains a carboxylic acid containing monomer, the resulting hybrid product may be converted to an amphoteric ion exchange resin by aminolysis and hydrolysis.

It is thus evident that a wide variety of adsorbents and ion exchange resins are envisaged in accordance with the invention. By selection of monomers, swelling solvents, crosslinking agents and Friedel-Crafts alkylating or acylating agents, polymers can be obtained with high surface

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area, high porosity, large pore size, good pore distribution, excellent physical stability and large particle size. These properties make the product suitable for liquid and gas phase separations and various other adsorbent and ion exchange applications. These include adsorption of organic materials such as phenol, carbon tetrachloride, hexane, cumene, and methyl chloroform.

We do not intend to be bound by theoretical considerations because the reasons for the exceptional adsorption capacities of the macronet polymer beads of the invention are not fully understood. Nevertheless we have observed that the best adsorbents are prepared from copolymers which exhibit the highest swelling ratios in a given solvent. For example, those copolymer beads which swell to 6-10 times their dry volume in ethylene dichloride may have adsorption capacities far exceeding those of conventional polymeric or carbon adsorbents with the same surface areas. A typical example is polymer beads prepared from styrene/divinylbenzene/acrylonitrile copolymer, monomer ratio 96/1.0/2.0, which is phase extended to macroreticular form with 28% by volume (of the organic phase) of methyl isobutyl carbinol. When swollen in ethylene dichloride and reacted under Friedel-Crafts conditions with poly-vinylchloride, the macronet product beads have a surface area of  $191 \text{ m}^2/\text{g}$  but have adsorption capacity equal to that of a non-macronet polymer of similar composition having a surface area of  $750 \text{ m}^2/\text{g}$ . The highly swollen condition which is then made permanent by the post-crosslinking reaction, in combination with the already high porosity and/or large pores of the macroreticular substrate, provides the exceptional adsorptive behaviour characteristic of the products of the invention.

The following examples further illustrate the invention. In the examples and indeed throughout this specification and claims, unless otherwise indicated, all parts and percentages are by weight, and the divinylbenzene is commercial quality, about 50% active, balance essential

all ethylvinylbenzene. The abbreviations have the following meanings:

- DVB - divinylbenzene
- S - styrene
- 5 PS - polystyrene
- VBC - vinylbenzyl chloride
- AN - acrylonitrile
- EDC - ethylene dichloride
- MIBC - methylisobutyl carbinol
- 10 PVC - polyvinylchloride
- CME - chloromethyl methyl ether
- SA - surface area
- XDC -  $\alpha,\alpha$ -dichloro-p-xylene
- TPC - terephthaloyl chloride
- 15 MDC - methylene dichloride
- NB - nitrobenzene
- MR - macroreticular
- DPE - diphenyl ether

EXAMPLE I

20 A. Preparation of Macroreticular Copolymer Beads

To a 5 dm<sup>3</sup>, 4-necked flask fitted with mechanical stirrer, reflux condenser, thermometer, nitrogen inlet, heating mantel, and thermowatch assembly was charged a premixed aqueous phase consisting of 1800 g. deionized  
25 water, 20 g boric acid, 0.87 g sodium nitrite 114 g poly (diallyl dimethyl ammonium chloride) dispersant, and 12.6 g Pharmagel (trademark) gelatine protective colloid. The stirring rate was preset at 125 rpm and a slow nitrogen flow (blanket) started. With agitator off, a  
30 premixed organic phase consisting of 500 g vinylbenzyl chloride, 450 g styrene, 315 g methylisobutyl carbinol (MIBC), 17.5 g of 54% divinylbenzene, 18.9 g acrylonitrile, 9.45 g benzoyl peroxide, and 0.653 g terpinoline was added. Agitation was started, the dispersion set by three  
35 on-off cycles and the mixture heated to 72°C for a period of 20 hours. The mixture was further heated to 100°C to remove MIBC through azeotropic distillation while maintaining a fluid dispersion by the addition of deionized water (0.5 dm<sup>3</sup>). On cooling, the suspension copolymer

beads were washed thoroughly with deionized water and oven dried at 80°C for 24 hours.

#### B. Preparation of Macronet Beads

To a 1 dm<sup>3</sup>, 3-necked flask fitted with mechanical stirrer, reflux condenser connected to a water scrubber, thermometer, and heating mantel was charged 31.2 g of the macroreticular copolymer beads of Part A, 26.25 g  $\alpha,\alpha$ -dichloro-p-xylene, and 0.3 dm<sup>3</sup> of ethylene dichloride. After standing about two days, the beads swelled to more than twice their initial volume. Then 54.0 g stannic chloride in 0.05 dm<sup>3</sup> of ethylene dichloride was added and the mixture heated to reflux for a period of 7.5 hours. On cooling, the reaction was quenched by dropwise addition of 0.3 dm<sup>3</sup> acetone with external cooling in a tap water bath. The solvents were removed by stick filtration, and the resin washed three times each with acetone, water, 10% HCl, water, and acetone. The product beads were then air dried followed by oven drying at 80°C for 16 hours (yield = 45.0 g). Analysis: 3.99% Cl, surface area = 1350 m<sup>2</sup>/g, porosity = 0.3638 cc/cc.

#### EXAMPLE 2

Substantially as described in Example 1, 31.2 g of commercially available macroreticular copolymer beads (S/DVB, 97/3) and 26.25 g  $\alpha,\alpha$ -dichloro-p-xylene swollen (20 hours) in 0.25 dm<sup>3</sup> ethylene dichloride was treated with 54.0 g stannic chloride in 0.05 dm<sup>3</sup> of ethylene dichloride and heated to reflux for 8.5 hours. Following quench, wash and isolation 46.1 g of oven dried beads were obtained. Analysis: 1.66% Cl, surface area = 445 m<sup>2</sup>/10<sup>-3</sup>kg, porosity = 0.3456 cc/cc.

#### EXAMPLE 3

Substantially as described in Example 1, to 25 g of macroreticular copolymer beads (S/DVB/AN, 96/2.0/2.0, phase extended with 28 vol. % MIBC) was added a solution of 14 g commercial PVC in 0.25 dm<sup>3</sup> EDC. The mixture was

heated for 16 hours, the swollen beads cooled, treated with 31.3 g of anhydrous  $\text{AlCl}_3$ , heated after 2 hours at  $25^\circ\text{C}$  to reflux and maintained at  $83^\circ\text{C}$  for 5 hours. The reaction was quenched as in Example 1, producing a product with a surface area of  $191 \text{ m}^2/\text{g}$ .

#### EXAMPLE 4

Substantially as described in Example 1, 106 g of macroreticular resin beads (S/DVB/AN, 96/2.0/2.0, phase extended with 51.3 vol. % toluene) was swelled over about 12 hours in a  $2 \text{ dm}^3$ , 3-necked flask with 1030 ml. of EDC. The flask was mounted in a toxic material hood and equipped with a condenser, Teflon blade stirrer,  $\text{N}_2$  inlet, two Claisen heads, two addition funnels and caustic CME scrubbers. CME (106 g., 1.32 mole) was added and the mixture was stirred for 45 min. at ambient temperature ( $\text{ca } 20^\circ\text{C}$ ). The mixture was then cooled to  $0^\circ\text{C}$ . After an additional 50 min at  $0^\circ\text{C}$ ,  $0.116 \text{ dm}^3$  (1 mole) of  $\text{SnCl}_4$  was added over a 20 min period, whereupon the mixture slowly turned black. The mixture was warmed to  $25^\circ\text{C}$  and stirred for 3 hours. It was then heated to reflux ( $85^\circ\text{C}$ ) and maintained at that temperature for 5 hours, then cooled and stirred overnight. The mixture was chilled to  $0^\circ\text{C}$  and  $0.5 \text{ dm}^3$  of MeOH was added slowly at  $0^\circ\text{C}$  over 2.5 hrs. to quench the reaction. The resin was stick filtered and treated successively with  $0.5 \text{ dm}^3$  MeOH, and  $0.5 \text{ dm}^3$  of 1N NaOH (cloudy supernatant), stick filtered and washed with water (resin pH = 11). Standard CME cleanup procedures (caustic wash) were used on filtrate solutions. The resin was backwashed in a graduate cylinder, then washed on a Buchner funnel with 1N HCl, deionized water (twice), 1:1 MeOH/water, and MeOH. After air and vacuum drying ( $50^\circ\text{C}$ ) the yield was 140.4 g (112% of theoretical). Microscopic examination showed clear dark amber, mainly whole beads,  $\text{SA} = 733 \text{ m}^2/\text{g}$ .

#### EXAMPLES 5-32

Table I below summarizes the compositions, reaction conditions and product characteristics of Examples 1 - 4

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as well as other preparations prepared substantially as described in Examples 1-4 with the changes indicated in the table. In all of the examples the extent of crosslinking of the macroreticular starting materials corresponds to the amount of crosslinking monomer. Thus, in Example 1, the MR composition is crosslinked to the extent of about 1% since the DVB is about 50% active, i.e. 0.5% of the composition. The analyses indicate the extraordinary adsorbency of the products since surface areas and porosities greatly exceed the 5 m<sup>2</sup>/g and 0.2 requirements for usefulness, respectively.

TABLE I

Ex.	MR Composition (%)	MR Amount (g)	Swelling Solvent $10^{-6}m^3$	Cross- linker (g)	Catalyst (g)
5	1 S/VBC/DVB(54%)/AN 45.6/50.7/1.8/1.9	31.2	EDC(300)	XDC (26.25)	SnCl <sub>4</sub> (54.0)
	2 S/DVB, 97/3	31.2	EDC(300)	XDC (26.5)	SnCl <sub>4</sub> (54.0)
	3 S/DVB/AN, 96/2.0/2.0		EDC	PVC	AlCl <sub>3</sub>
10	4 (S/DVB/AN) <sup>1</sup> 96/2.0/2.0		EDC	CME	SnCl <sub>4</sub>
	5 S/DVB, 96/4	10.4	EDC(75)	XDC (17.5)	SnCl <sub>4</sub> (34.0)
	6 S/DVB, 96/4	31.2	EDC(300)	XDC (52.5)	SnCl <sub>4</sub> (54.0)
15	7 S/DVB, 96/4	31.2	EDC(300)	XDC (52.5)	SnCl <sub>4</sub> (30.0)
	8 S/DVB, 96/4	31.2	EDC(300)	XDC (52.5)	SnCl <sub>4</sub> (15.0)

20 <sup>1</sup> Phase extended with toluene (51.4%).



TABLE I Continued

<u>Reaction Conditions</u>			<u>ANALYSIS</u>				
	Temp.	Time.			SA	Porosity	
Ex.	(°C.)	(Hrs.)	% Cl	% S	(m <sup>2</sup> /g.)	m <sup>3</sup> /m <sup>3</sup> (Dry)	
5	1	83	7.5	3.99	-	1349.9	0.3638
	2	83	8.5	1.66	-	445.2	0.3456
	3	83	5.0			191	
	4	85	5.0			733.5	
	5	83	4.5	1.9	-	404.5	0.75
10	6	83	7.0	2.1	-	424.8	0.5086
	7	83	7.5	1.95	-	367.8	0.6187
	8	83	7.5	2.1	-	262.5	0.5677

TABLE I Continued

Ex.	MR		MR Amount (g)	Swelling Solvent 10 <sup>-6</sup> m <sup>3</sup>	Cross- linker (g)	Catalyst (g)
	Composition					
5	9	S/DVB, 96/4	31.2	EDC(300)	XDC (52.5)	SnCl <sub>4</sub> (8.0)
	10	S/DVB, 96/4	31.2	EDC(300)	XDC (52.5)	SnCl <sub>4</sub> (8.0)
	11	S/DVB, 96/4	31.2	EDC(300)	TPC (60.9)	SnCl <sub>4</sub> (78.15)
10	11a	S/DVB, 96/4	31.2	EDC(200)	XDC (52.5)	SnCl <sub>4</sub> (15.0)
	12	S/DVB, 96/4	31.2	EDC(300)	XDC (26.25)	SnCl <sub>4</sub> (15.0)
	13	S/DVB, 96/4	31.2	NB (300)	XDC (26.25)	AlCl <sub>3</sub> (40.0)
15	14	S/DVB, 96/4	31.2	EDC(200) NB (100)	TPC (30.45)	AlCl <sub>3</sub> (40.0)
	15	S/DVB, 97/3	31.2	EDC(300)	XDC (52.5)	SnCl <sub>4</sub> (54.0)
	20					

TABLE I Continued

Reaction Conditions				ANALYSIS			
Ex.	Temp. (°C.)	Time (Hrs.)	% Cl	% S	SA (m. <sup>2</sup> /g.)	Porosity m <sup>3</sup> /m <sup>3</sup> (Dry)	
5	9	83	7.5	1.2	-	143.4	0.5705
	10	83	24.0	2.5	-	262.1	0.5738
	11	83	7.5	0.5	-	44.6	0.5262
	11a	83	7.5	2.2	-	394.2	0.4939
	12	83	7.5	1.8	-	160.8	0.6174
10	13	90	7.5	0.72	-	150.9	0.5436
	14	90	7.5	0.52	-	137.2	0.5324
	15	83	6.5	-	-	441.7	0.3014

TABLE I Continued

Ex.	MR Composition (%)	MR Amount (g.)	Swelling Solvent $10^{-6}m^3$	Cross- linker (g.)	Catalyst (g.)
5	16 S/DVB, 97/3	31.2	NB (300)	TPC (30.45)	$AlCl_3$ (40.0)
	17 S/DVB, 97/3	31.2	EDC(300)	$S_2Cl_2$ (20.25)	$SnCl_4$ (54.0)
	18 S/DVB, 97/3	31.2	EDC(200)	$S_2Cl_2$ (20.25)	$AlCl_3$ (40.0)
10	19 S/DVB, 97/3	31.2	NB (100)	TPC (30.45)	$FeCl_3$ (50.0)
	20 S/DVB, 97/3	31.2	EDC(200)	$SCl_2$ (15.45)	$AlCl_3$ (40.0)
	21 S/DVB, 97/3	31.2	NB (300)	$SCl_2$ (15.45)	$AlCl_3$ (40.0)
15	22 S/DVB, 97/3	31.2	EDC(200)	NB (100) MDC 0.1dm <sup>3</sup>	$AlCl_3$ (40.0)
	23 Same as example 1	31.2	EDC(300)	$S_2Cl_2$	$AlCl_3$
			NB (100)	(20.25)	(40.0)
20					

TABLE I Continued

<u>Reaction Conditions</u>			<u>ANALYSIS</u>				
	Temp.	Time			SA	Porosity	
5	Ex. (°C.)	(Hrs.)	% Cl	% S	(m. <sup>2</sup> /g.)	m <sup>3</sup> /m <sup>3</sup> (Dry)	
	16	90	8.5	1.10	-	133.2	0.2518
	17	65 - 75	5.0	3.03	21.5	79.2	0.3294
	18	78	7.0	2.59	19.72	134.1	0.4615
	19	85 - 90	7.5	0.64	-	78.4	0.3581
10	20	20	RT	3.78	8.69	53.5	0.4090
	4	85-90					
	21	20	RT	4.29	12.63	83.2	0.4572
	4	85-90					
	22	40 - 50	7.5	0.06	-	84.0	0.3153
15	23	85	7.5	4.92	12.63	134.1	0.4615

TABLE I Continued

Ex.	MR Composition (%)	MR Amount (g.)	Swelling Solvent $10^{-6} \text{ m}^3$	Cross- linker (g.)	Catalyst (g.)
5	24	Same as Example 1	31.2	EDC(400)	$\text{SnCl}_4$ (15.45) (54.0)
	25	Same as Example 1	31.2	NB (300)	MDC $0.1 \text{ dm}^3$ (40.0)
	26	Same as Example 1	31.2	EDC(300)	XDC (26.25) (54.0)
	26a	Same as Example 1	31.2	EDC(300)	XDC (26.25) (54.0)
	27	VBC/DVB (54%)90/10	50	NB (200)	$\text{CHCl}_3$ $0.2 \text{ dm}^3$ (133)
15	28	S/DVB 97/3	38.53	EDC(300)	$\text{CHCl}_3$ (110) (67)
	29	S/DVB 97/3	38.53	$\text{CCl}_4$ (300)	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ $\text{AlCl}_3$ (67)

TABLE I Continued

		Reaction Conditions		ANALYSIS			
		Temp.	Time			SA	Porosity
Ex.	( C.)	(Hrs.)	% Cl	% S	(m. <sup>2</sup> /g.)	m <sup>3</sup> /m <sup>3</sup> (Dry)	
5	24	RT	20	8 76	12.26	98.1	0.0827
		85	4				
	25	40 - 50	7.5	0.95	-	445.1	0.2767
	26	83	7.5	13.97	-	950.7	0.4124
	26a	83	7.5	-	-	920.5	0.4083
10	27	90	8.0	-	-	358	-
	28	83	8.0	-	-	68	-
	29	80	8.0	-	-	9.6	-

TABLE I Continued

Ex.	MR Composition (%)	MR Amount (g.)	Swelling Solvent $10^{-6}m^3$	Cross- linker (g.)	Catalyst (g.)
5	30 (VT/DVB/AN) <sup>2</sup> 95/2.4/2.6	50	EDC(900)	XDC (38.5)	SnCl <sub>4</sub> (114.7)
	31 (VBC/DVB/AN) <sup>3</sup> 97/1/2	50	EDC(800)	DPE (13.3)	SnCl <sub>4</sub> (86)
10	32 (S/DVB/AN) <sup>4</sup> 96.3/1.8/1.9	50	EDC(800)	CCl <sub>4</sub> (73.7)	AlCl <sub>3</sub> (64.02)

<sup>2</sup> Phase extended with toluene (200 parts)

<sup>3</sup> Phase extended with MIBC (498 parts)

20 <sup>4</sup> Phase extended with MIBC (111.9 parts)



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TABLE I Continued

5	<u>Reaction Conditions</u>			<u>ANALYSIS</u>		
	Ex.	Temp. (°C.)	Time (Hrs.)	% Cl	% S SA (m. <sup>2</sup> /g.)	Porosity m <sup>3</sup> /m <sup>3</sup> (Dry)
	30	82	5.0	-	- 15.6	-
	31	82	5.0	-	- 300.7	-
	32	Reflux	4.0	-	- 72.6	-

### PERFORMANCE EVALUATIONS

Certain of the macronet polymers of Table I above were evaluated for adsorption of phenol, carbon tetrachloride/Hexane, cumene- and methylchloroform. Table II reports columnar loading studies using solutions containing 6300 ppm. Phenol as compared with a commercially available /S/DVB macroreticular adsorbent not of the macronet type. It will be noted that the product of Example 1 exhibited 19% improvement in capacity over the commercial adsorbent.

TABLE II

Phenol Adsorption			
Adsorbent	Capacity (g./dm <sup>3</sup> )	Capacity Change (g./dm <sup>3</sup> )	Change (%)
Commercial S/DVB	80	--	--
Example 1	95	+15	+19

Certain of the macronet beads of the invention (Table I above) were also evaluated for CCl<sub>4</sub> and hexane vapor phase adsorption by determining weight gain of the resin samples subjected to an environment of an excess of either adsorbate in hexadecane in a closed container for 24 hours. Table III reports the results as wt.% CCl<sub>4</sub> or hexane adsorbed as compared with three brands of activated carbon and three types of commercially available S/DVB adsorbent resins not of the macronet type. It will be noted that certain of the adsorbents of the invention proved to be better than the carbon adsorbents.

TABLE III

CCl<sub>4</sub>/Hexane Adsorption

	<u>Adsorbent</u>	<u>Wt. % CCl<sub>4</sub></u>	<u>Wt. % Hexane</u>
	BPC Activated Carbon	60-65	25
5	Witco 517 Activated Carbon	60	28
	PCB Activated Carbon	60	--
	Commercial S/DVB	56	28.1
<hr/>			
10	Example 1	97	42
	Example 26	91	42
	Example 2	51	24
	Example 11a	52	24
	Example 31	68.8	25.6
15	Example 4	79.8	38.0

Table IV reports column loading for cumene and methylchloroform in the vapor phase as compared with a commercially available S/DVB non-macronet adsorbent. It will be noted that the Example 4 sample adsorbed cumene more than 90%. In the methylchloroform loading studies, the Example 2 sample gave 84% pickup and the Example 26 sample gave 94% pickup. In the same studies it will be noted that adsorption from a high concentration adsorbate (C<sub>0</sub> = 369,500 ppm.) was also excellent.

TABLE IV

CUMENE/METHYLCHLOROFORM (MCF) ADSORPTION

	<u>Adsorbent</u> <u>Example</u>	<u>Sample Wt. (g.)</u>		<u>C<sub>2</sub>(ppm.)<sup>1</sup></u>	
		<u>MCF</u>	<u>Cumene</u>	<u>MCF</u>	<u>Cumene</u>
5	26	0.5017	-	23,100	-
	2	0.4639	-	23,100	-
	26a	0.5018	-	23,100	-
	Commercial				
	S/DVB(Control)	-	-	23,100	-
10	26a	3.0013	-	369,500	-
	4	3.0016	-	369,500	-
	Commercial				
	S/DVB(Control)	-	-	369,500	-
15	26a	-	3.0006	-	703,870
	32	-	3.0024	-	703,870
	3	-	3.0028	-	703,870
	4	-	5.0017	-	1,353,600
20	Commercial				
	S/DVB (Control)	-	-	-	703,870

<sup>1</sup> Initial concentration of adsorbate

TABLE IV Continued

CUMENE/METHYLCHLOROFORM (MCF) ADSORPTION

	Adsorbent	Ceq. (ppm.) <sup>2</sup>		Capacity (mg./g.)	
		MCF	Cumene	MCF	Cumene
5	Example				
	26	112	-	65	-
	2	3847	-	59	-
	26a	700	-	63	-
	Commercial				
10	S/DVB(Control)	110	-	30	-
	26a	2880	-	174	-
	4	2880	-	170	-
	Commercial				
15	S/DVB(Control)	2000	-	100	-
	26a	-	570	-	300
	32	-	460	-	300
	3	-	1160	-	300
20	4	-	1168	-	350
	Commercial				
	S/DVB(Control)	-	1160	-	380
25					

<sup>2</sup> Concentration of adsorbate at equilibrium after treatment with adsorbent.

CLAIMS:

1. A synthetic polymeric adsorbent comprising lightly crosslinked macroreticular copolymer beads containing units of aromatic monomer, said beads being crosslinked after formation and in a swollen state with one or more of the following crosslinkers: polyfunctional alkylating agents, polyfunctional acylating agents, sulfur halides.
2. An adsorbent as claimed in Claim 1 wherein the aromatic copolymer is a copolymer of styrene and divinylbenzene and/or vinylbenzylchloride and, optionally acrylonitrile.
3. An adsorbent as claimed in Claim 1 or 2 wherein the lightly crosslinked copolymer contains 0.25 to 20% by weight crosslinker units.
4. An adsorbent as claimed in any preceding claim wherein the crosslinker is one or more of the following: sulfur monochloride, sulfur dichloride,  $\alpha,\alpha$ -dichlorop-xylene, terephthaloyl chloride, polyfunctional alkylating agents having halogen, hydroxyl, olefin and/or epoxy functionality.
5. An ion exchange resin comprising synthetic polymeric beads as claimed in any preceeding claim carrying ion exchange functional groups.
6. A process for making a synthetic polymeric adsorbent which comprises swelling lightly crosslinked macroreticular copolymer beads containing units of aromatic monomer in an inert organic solvent and crosslinking the swollen beads in the presence of Friedel-Crafts catalyst with one or more of the following crosslinkers: polyfunctional alkylating agents, polyfunctional acylating agents, sulfur halides.
7. A process as claimed in Claim 6 as applied to the preparation of adsorbent as claimed in any one of Claims 2 to 5.
8. A process for the preparation of ion exchange resin which comprises carrying out a process as claimed in Claim 6 or 7 and treating the beads so produced to impart ion exchange functional groups thereto.

9. A process for removing a dissolved component from a fluid by adsorption which comprises contacting the fluid with adsorbent as claimed in any of Claims 1 to 4.
- 5 10. An ion exchange process wherein a fluid is contacted with an ion exchange resin as claimed in Claim 5.
11. A catalytic process wherein an ion exchange resin as claimed in Claim 5 is used as catalyst.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

EP 79 30 1463

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages		
	<u>US - A - 3 997 706</u> (L. GALEAZZI) * Claims * --	1	B 01 J 39/08 C 08 F 212/14 C 08 F 8/00
	<u>US - A - 3 586 644</u> (G.J. DE JONG) * Claims * --	1-4	
	<u>US - A - 4 093 567</u> (M.J. HURWITZ et al.) * Claims * ----	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 1)  B 01 J 39/08 C 08 F 212/14 C 08 F 8/00 8/02 8/10 8/34
			CATEGORY OF CITED DOCUMENTS  X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons  &: member of the same patent family. corresponding document
The present search report has been drawn up for all claims			
Place of search  The Hague		Date of completion of the search  22-10-1979	Examiner  FOUQUIER